Global Atmosphere Watch
World Calibration Centre for Surface Ozone
and Carbon Monoxide

Swiss Federal Laboratories for Materials Testing
and Research (EMPA)

EMPA-WCC REPORT 98/7

Submitted to the

World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT

SURFACE OZONE and CARBON MONOXIDE

GLOBAL GAW STATION CAPE POINT

SOUTH AFRICA, SEPTEMBER 1998

Submitted by

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1. Abstract

A system and performance audit was conducted by the World Calibration Centre for Surface Ozone and Carbon Monoxide at the global GAW station Cape Point, South Africa. Below, the findings, comments and recommendations are summarised:

Air Inlet System:

The new inlet system, concerning construction materials as well as residence time, is adequate for gas analysis and fulfils the recommendations about inlet systems of the WMO-GAW Report No. 97.

Instrumentation:

Ozone: The measurement technique used is the UV-method, which is the preferred method in the GAW programme. The operation of two ozone analysers in parallel (basic and backup instrument) considerably increases confidence in data quality and becomes even more important since an ozone calibrator is not permanently available at the site.

CO / gas standards: The gas chromatography technique followed by mercury reduction detection, as operated at Cape Point, is a widely-used method for background air measurements. Applied with care it is characterised by excellent specificity, very low detection limits and high precision (WMO-GAW report No. 98). However, attention should be given to the relation between detector signal and concentration (non-linearity over an expanded mixing ratio) of the actual configuration. The analyser RGA-3, although in operation for around 10 years, is in good condition.
The very frequent checks of the system with a working standard and the daily stability check with a CMDL standard, both within the relevant range of the site, validate the measurements. All measurement values are based on the IFU standards but the traceability to CMDL standards is still guaranteed.

Operation and Maintenance:

The appearance of the station is clean and functional.

Ozone: One of the main factors of quality assurance is the regular intercomparison by multipoint calibration between the analysers and an ozone reference (transfer standard) that is traceable to the NIST. The purchase of such an instrument would certainly progress the entire measurements and is therefore very desirable.
Maintenance that is carried out on a case by case basis has its advantage over following a strict schedule due to the fact that there is no unnecessary interruption of the instruments. Since the required experience for such a practice is present we do not recommend any change to this procedure.

CO: Because of the operators experience with gas chromatography, the maintenance is carried out on a case by case basis. The check of some analyser test points and controlling chromatograms gives the operator enough information about the state of the instrument to determine if maintenance is necessary. When the modem connection is realised finally, this control can be even intensified.

Data Handling:

Ozone: The procedure of data treatment is well organised and clearly arranged and will be even more improved with the new acquisition system. Any recalculation can easily be traced back to the raw values. The reprocessing of the data is done on a regular monthly interval, i.e. irregularities can be detected early. Reviewing of the final data set by two persons is welcome, since this measure increases the reliability of the data.
The long awaited direct data transfer via modem has been still not possible but is expected to be realised within the next few months.

<u>CO</u>: The procedure of data treatment is well organised and clearly arranged and similar to the ozone measurements. Since mid-1997 raw data including chromatograms are being archived on CD on a monthly basis. This welcomed effort makes it possible for chromatograms to be reintegrated in the future.

The available data should be sent to the WDC for greenhouse gases as soon as calibration queries and quality assurance issues have been settled.

Documentation:

The documentation of the ozone and CO measurements meets all the requirements of the GAW guidelines. As pointed out already during the last audit, it would be very desirable to have a practice orientated SOP for maintenance and operation, as a preventive measure to avoid loss of accumulated knowledge due to personnel changes.

Competence:

All persons associated directly or indirectly with the operation of the station are highly motivated and experts in their fields. Obviously, due to long-standing experience of Mr E. Brunke and also the adequate way he is handing over know-how to new staff, the operators are very familiar with the techniques and problems connected with ozone and CO measurements.

The invaluable support of the IFU, Garmisch, as a strong twinning partner should be especially mentioned as this work contributes an important part to the success of the station.

Ozone Intercomparisons:

The ozone concentration observed at Cape Point (1997) usually ranged between 12 and 32 ppb (5- and 95-percentile of hourly mean values). The basic and the backup instruments fulfil the assessment criteria as "good" over the tested and relevant range up to 100 ppb (figures 1 and 2).
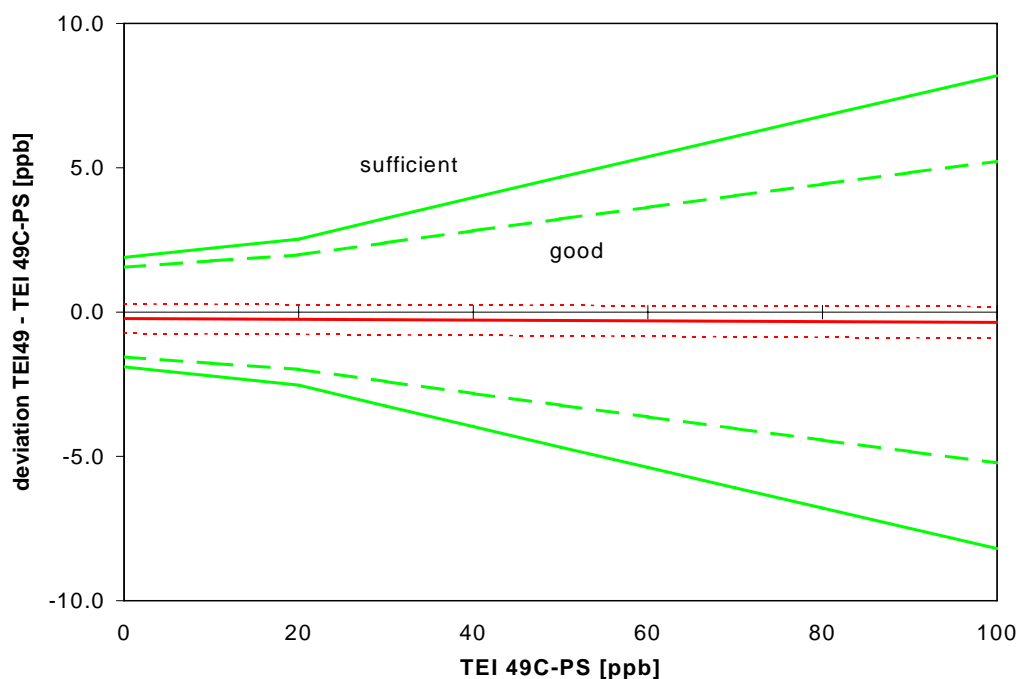
Figure   1: Intercomparison of ozone instrument TEI 49 (linear regression with prediction interval 95%)
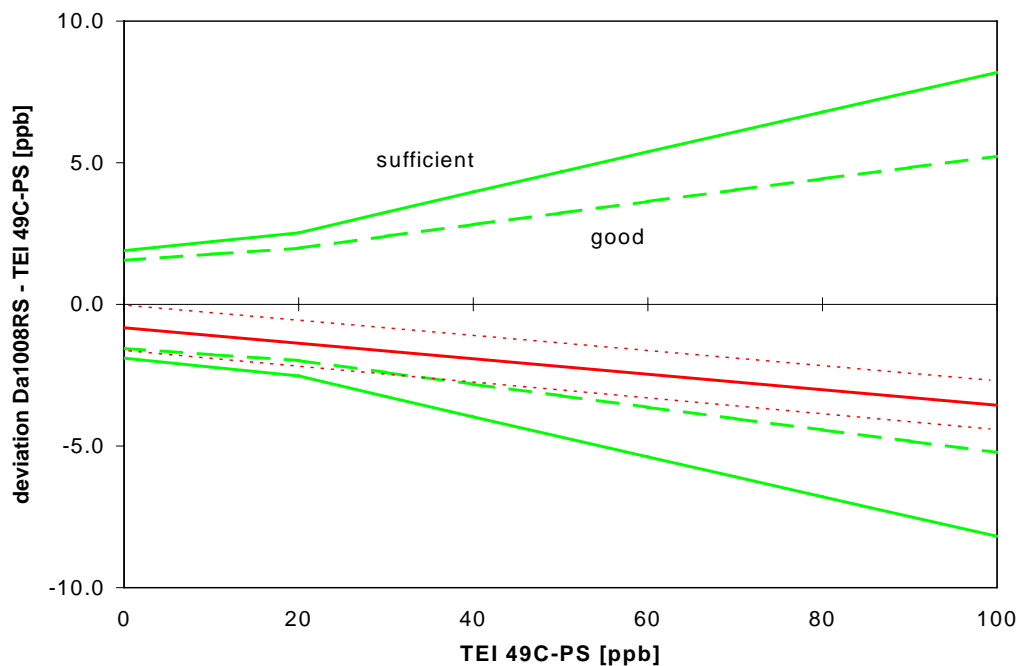
Figure 2: Intercomparison of ozone instrument Dasibi 1008RS (linear regression with prediction interval 95%)

Carbon Monoxide Intercomparisons:

The CO (RGA-3 gas chromatograph) results of the site deviate quite substantially from the conventional true values of the transfer standards by EMPA. Partly, this deviation can be explained by the applied calibration procedure of the station (performing a single point of the RGA-3 system and referring to the IFU scale). However, another possibility that should be considered is that a standard cylinder could have altered. As a consequence of the noted discrepancy between the EMPA transfer standards and the station standards (all of them are CMDL certified), EMPA will follow up the findings and inform the station operators. Thus, for the moment we do not recommend any data adjustment.

For the next audit exercise, it is planned to provide more CO transfer standards in the low ppb range in order for a better coverage of the station's relevant range of CO.

Figure 3: Intercomparison of CO gas chromatograph RGA-3

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Dübendorf, 26. April 1999   Dübendorf, EMPA-WCC

Project engineer   Project manager

A. Herzog   B. Buchmann

Technical expert, S. Bugmann

2. Introduction

In establishing a co-ordinated quality assurance programme for the WMO Global Atmosphere Watch programme, the air pollution and environmental technology section of the Swiss Federal Laboratories for Materials Testing and Research (EMPA) was assigned by the WMO to operate the WMO-GAW World Calibration Centre (WCC) for Surface Ozone and Carbon Monoxide. At the beginning of 1996 our work had started within the GAW programme with the parameter surface ozone. The activities were extended to carbon monoxide in the middle of the year 1997. The detailed goals and tasks of the WCC concerning surface ozone are described in the WMO-GAW report No. 104.

In agreement with the responsible persons in charge of O_3 and CO measurements at the Cape Point Atmospheric Trace Gas Research Station, the second system and performance audit was conducted. The station is operated by the South African Weather Bureau and is an established site for long-term measurements of several chemical compounds and physical and meteorological parameters for background, clean air, conditions. Its location in the Southern Hemisphere, with only few stations, makes it additionally valuable for scientific research investigating the global climate south of the equator.

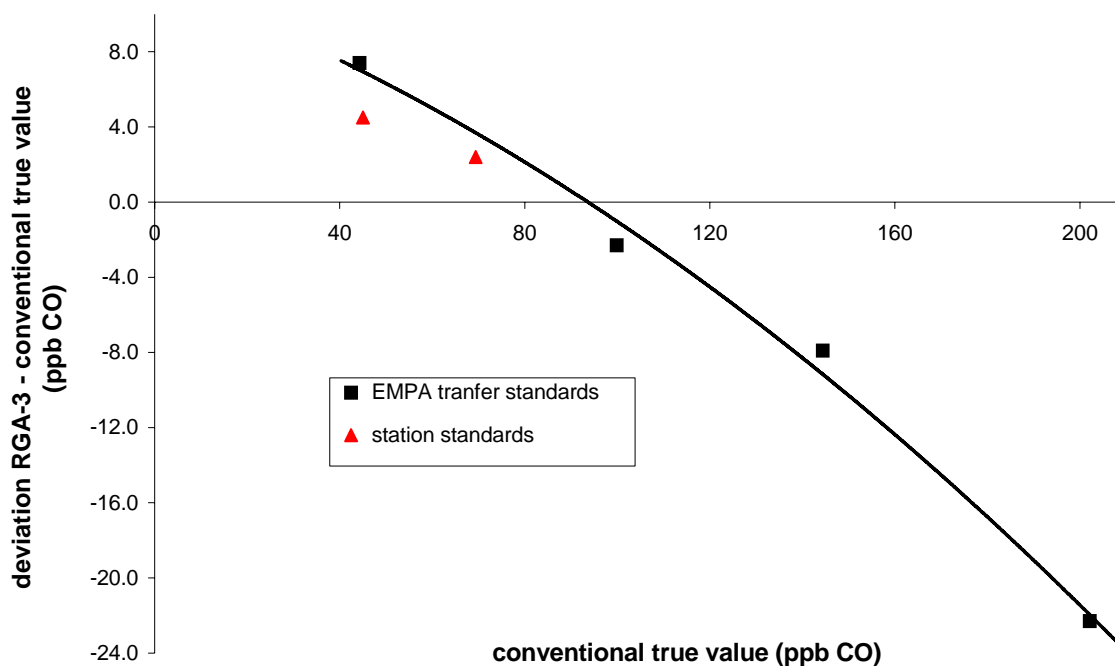The scope of the audit which took place from September 6 to 11, 1998, was confined to the surface ozone and carbon monoxide measurements. The entire process, beginning with the inlet system and continuing up to the data processing, and also the supporting measures of quality assurance, were inspected during the audit. The audit concerning ozone was performed according to the "Standard Operating Procedure (SOP) for performance auditing ozone analysers at global and regional WMO-GAW sites", WMO-GAW Report No. 97. No Standard Operation Procedures (SOP) have been established for CO measurements by QA/SAC until now. For this reason, the ozone SOP was adapted for carbon monoxide. The assessment criteria for the ozone intercomparison have been developed by EMPA and are based on WMO-GAW Report No. 97 (EMPA-WCC report 98/5 "Traceability, Uncertainty and Assessment Criteria of ground based Ozone Measurements" by P. Hofer, B. Buchmann and A. Herzog, September 1998, available on request from the authors at: EMPA, 134, Ueberlandstr. 129, CH-8600 Dübendorf).

The present audit report is submitted to the station manager and involved persons, the World Meteorological Organization in Geneva and the Quality Assurance and Scientific Activity Centre (QA / SAC) for Europe and Africa.

Audits that had previously been performed:

- October 1995 by the QA / SAC for Europe and Africa, "System Audit GAW Station Cape Point, Republic of South Africa", Dr. F. Slemr

- January 1997 by the EMPA-WCC, "System and performance audit for surface ozone, global GAW station Cape Point, South Africa", A. Herzog, B. Buchmann, P. Hofer

System and performance audits at global GAW stations will be regularly conducted on mutual arrangement.

3. Global GAW Site Cape Point

3.1. Site Characteristics

The Cape Point station is located in a nature reserve at the southern end of the Cape Peninsula, South Africa, (coordinates: 34°21' S, 18°29' E). The monitoring station is exposed to the sea on top of a cliff 230 m a.s.l., about 60 km south from the city of Cape Town. Since the dominant wind direction is SE - S - SW, the station is subjected to maritime air from the South Atlantic most of the time. Due to its very special location on a peninsula extremity, the vicinity around Cape Point (sector larger than 300°) is primarily ocean and the only ground in the surrounding area consists of sparsely vegetated rock.

In 1995, the station moved from the two former lighthouse cottages to a newly built one story measurement station. The new location provides excellent space for present and future measurement activities and underlines the importance given to the site by the Government. It is situated adjoining the old station beneath the 30 m sampling tower and is built partially into the rock. The air inlet and several pieces of meteorological equipment are mounted on a platform at the top of the flat roof.

In the last few years the Cape Point area has developed into a major tourist attraction with hundreds of daily visitors from Cape Town arriving by cars and busses. About 650 m north-west of the station a large parking lot was built for the public traffic. From there, the station is approximately 150 m above and is reached by an electrical funicular. The tourists visit Cape Point mainly between 09:30 and 17:30 during the day. No tourists are permitted in the reserve after sunset so that no people and vehicles are present on the lower parking lot at night. Up to now, only a few Mini-busses and the station operators are permitted to travel up the steep drive to the station. Since the developing process will continue one should be aware that scientific interests need to be met in spite of increased tourism.

Since the last audit, the near environment of the site has not changed in a way that could have influenced the ozone or carbon monoxide measurements significantly.

Figure 4: Picture of the station Cape Point
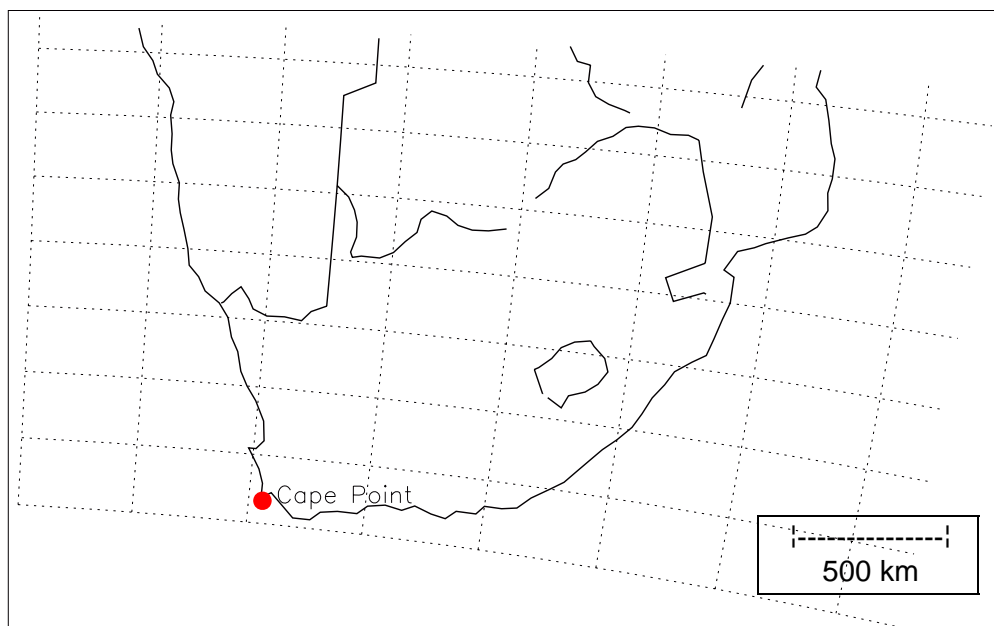
Figure 5: Map of southern Africa

3.2. Operators

The Atmospheric Trace Gas Research Station at Cape Point was set up in 1978 and was operated until 1998 by the Earth Marine and Atmospheric Sciences Division of the CSIR in co-operation with the Fraunhofer Institute for Atmospheric Environmental Research (IFU). Today, the South African Weather Bureau (SAWB) has taken over the staff and the operational responsibility for the site. The Fraunhofer Institute for Atmospheric Research (IFU) still is the twinning partner which supplies much of the instrumentation and supporting material and assists the station operators in QA matters.

Mr E.-G. Brunke, who is in charge of the operation of the Atmospheric Trace Gas Research Station at Cape Point, directs a team of three co-workers. The structure of the station management at Cape Point is shown in Table 1.

Table 1: Operators

Mr Ernst-Guenther Brunke, Officer-in-charge
Operators Mr Danie van der Spuy, Electronical engineer Mr Casper Labuschagne, Atmospheric chemist Mr Bhawoodien Parker, Meteorologist
External expert Dr H.E. Scheel, IFU, Garmisch-Partenkirchen (D) Scientific consultant

All persons associated directly or indirectly with the operation of the station are highly motivated and experts in their fields. Obviously, due to long-standing experience of Mr E. Brunke and also the adequate way he is handing over know-how to new staff, the operators are very familiar with the techniques and problems connected with ozone and CO measurements.

The invaluable support of the IFU, Garmisch, as a strong twinning partner should be especially mentioned as this work contributes an important part to the success of the station.

3.3. Ozone Level

The site characteristics and the relevant ozone concentration range can be well described by the frequency distribution. In figure 6 the frequency distribution of the filtered hourly mean values for the year 1996 is shown. The relevant ozone concentrations were calculated ranging between 12.1 and 31.5 ppb, according the 5- and 95-percentile of the hourly mean values respectively. The annual mean of the background data (filtered) was 22.7 ppb.

Source of data: E.-G. Brunke

Figure 6: Frequency distribution of the filtered hourly mean values of the ozone mixing ratio (ppb) at Cape Point for the year 1996. Capture of filtered data was 80 per cent (total capture: 93.5%)

3.4. Carbon Monoxide Level

The relevant carbon monoxide concentration range can be well defined by the frequency distribution. In figure 7 the frequency distribution of the filtered hourly mean values for the year 1996 is shown. The relevant carbon monoxide concentrations were calculated, ranging between 39.7 and 64.1 ppb, according the 5 and 95 percentile values respectively. The annual background data capture of carbon monoxide was about 60 %. The annual mean was 51.9 ppb.
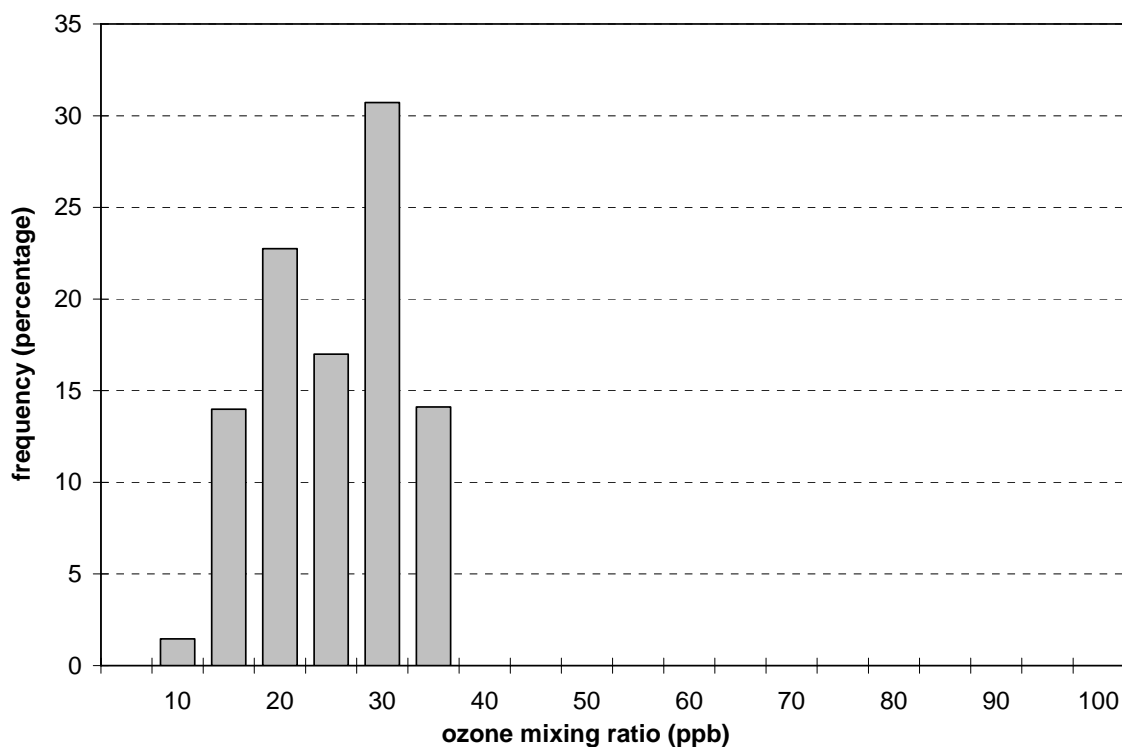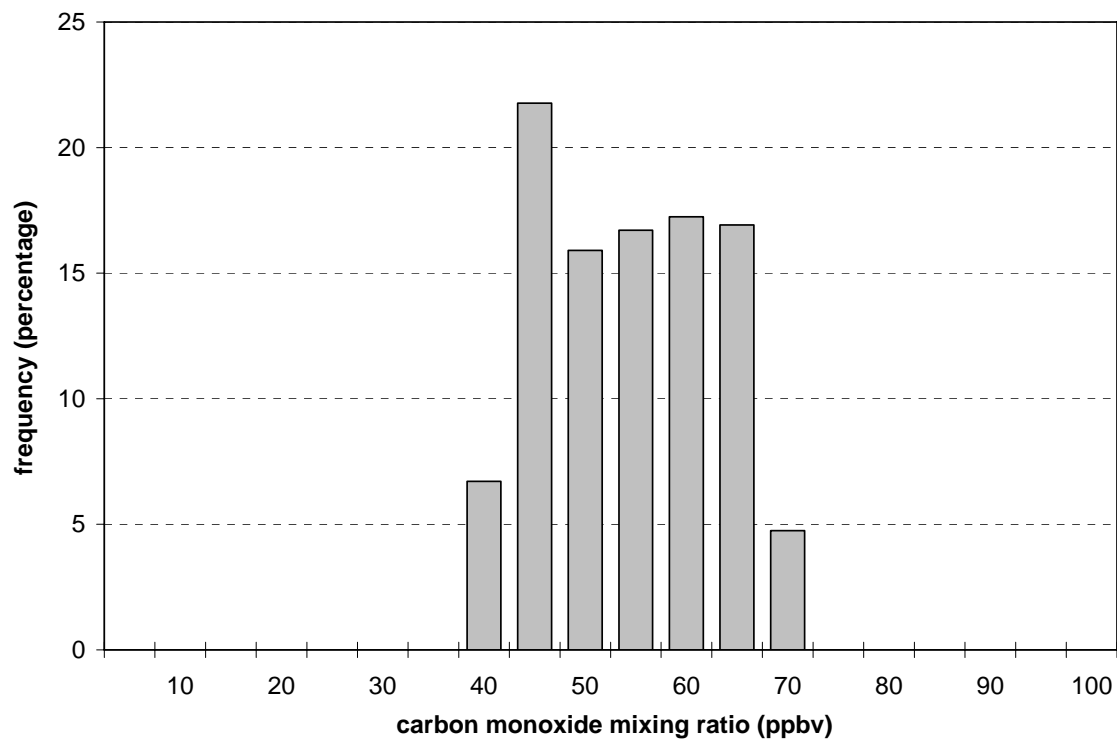
Source of data: E.-G. Brunke

Figure 7: Frequency distribution of the hourly mean values of the carbon monoxide mixing ratio (ppb) at Cape Point for the year 1996. Capture of filtered data was 60 per cent (total capture: 91.3%).

4. Measurement Techniques

4.1. Surface Ozone

4.1.1. Air Inlet System for Ozone

In November 1996 a new air inlet system was taken in use and is now the actual system. It is mounted on the flat roof of the laboratory tower. The inlet part of the system on the flat roof consists of an inverse stainless steel bucket shielding the system from rain and is stacked on a stainless steel tube (100 mm i.d., 4.3 m long) that surrounds an internal SCHOTT glass tube (50 mm o.d.). The glass tube leads straight through a hole in the ceiling into the laboratory building connected to a SCHOTT glass manifold indoors (80 mm i.d., 40 cm long). It is continuously flushed at 1.5 m^3 per minute with ambient air. For the ozone measurements, a PFA Teflon tube (4 mm i.d., 1.5 m long) branches off from the glass manifold leading to the ozone analyser that is a TEI 49. The sample pump of the analyser is being used to draw ambient air through this Teflon tube according to the instrument's specified internal flow. The instrument is further protected from dust and particles with a Teflon inlet filter. The total residence time of the ambient air, through the inlet line to the instrument, is about 2 seconds. The basic instrument TEI 49 is permanently connected to the new inlet while the backup analyser Dasibi 1008RS alternately switches between the new and the former system in a one hour interval.

The former inlet system is located at the top of a 30 m high sampling tower. Thus the air sample has to pass through a 43 m long 1/4" PFA tube and a metal below pump before reaching the analysers (10s residence time). The old system is still used because the operators are performing systematic cross checks to compare data obtained from the 4 m inlet system with those from the 30 m mast aiming to make a potential "back correction" to the historical data set possible. The third instrument, Dasibi 1008PC, is permanently connected to the former inlet.

Comments

The new inlet system, concerning construction materials as well as residence time, is adequate for gas analysis and fulfils the recommendations about inlet systems of the WMO-GAW Report No. 97.

4.1.2. Instrumentation, Ozone Analysers

The instruments are installed in racks in the spacious room of the laboratory building that is equipped with a ventilation system (high volume fan). Normal temperature is around 22°C, nevertheless, on a sunny hot day a temperature raise of about 4°C can be observed. The analysers are protected from direct sunlight. In the same room is the CO system.

The instrumentation used for measuring ozone at Cape Point during second audit was identical with the configuration during the last audit in January 1997 and is shown below in table 2.

The ozone analyser TEI 49 is the basic instrument since January 1997 and is supported by the backup instrument Dasibi 1008RS. To investigate the potential difference between the actual and the original inlet line (30 m mast) the Dasibi 1008RS switches between the two inlet systems, every hour. In addition, a third ozone analyser, the Dasibi 1008PC, is continuously analysing air from the 30 m mast. The results of the intercomparison of the Dasibi 1008PC are listed in the appendix ozone.

Table 2: Ozone field instruments

type	TEI 49 #51594-288	Dasibi 1008RS #4840
method	UV absorption	UV absorption
usage	basic instrument	backup instrument
at Cape Point	since August 1996	since 1991
range	0-1000 ppb	0-1000 ppb
analog output	0-10 V	0-10 V
electronic offset	56	0 (units)
electronic coeff.	507	307 (absorption coeff.)
instrument's specials	- at new air inlet - internal ozone generator	- alternatively at new and original air inlet - connected to an external ozone generator

For the TEI 49 another zero air unit consisting of an oil-free-compressor, molecular sieve and activated charcoal is used in combination with the internal TEI ozone generator to perform the daily zero and span checks (50 ppb).

For the daily zero checks of the two Dasibi instruments ambient air is simply drawn through an externally installed Dasibi scrubber (MnO_2) and splitted to the instruments. These checks are automatically triggered at midnight by an IFU constructed unit, which also includes an ozone generator.

Comments

The measurement technique used is the UV-method which is the preferred method in the GAW programme. The operation of two ozone analysers in parallel (basic and backup instrument) considerably increases confidence in data quality and becomes even more important since an ozone calibrator is not permanently available at the site.

4.1.3. Operation and Maintenance, Ozone

Preventive maintenance of the instruments includes adjustment of the pressure transducers and exchanging of the teflon inlet filters, and is performed on a case by case basis (every 2-6 month). About once a year the instrument glass cells are cleaned.

For both Dasibi instruments an automatic zero and span check at midnight is triggered with an IFU constructed unit including an ozone generator. From the results of the zero point checks of a month, an average offset is calculated and subtracted from the whole data set. The span check is intended to have only confirming character and is not used to correct the data set.

Automatic zero and span checks are made as a daily check of the TEI 49 analyser. At midnight, a span check (50 ppb) is made for about 15 minutes as a routine check of the ozone analyser. These data are not used for correcting the ambient air measurement values because the precision and stability of ozone generators would be generally too poor to be used for calibration purposes.

At the same time, a zero check is performed. Later on, the data is used for zero correction of O_3 mixing ratios.

Regular multipoint calibrations of the analysers can not be carried out, because there is no ozone calibrator for reference that is traceable to the NIST, at Cape Point. Every few years, a transfer standard is shipped from IFU, Germany, to Cape Point to perform a calibration. An accuracy check of a kind, i.e. long-term parallel measurements of ambient air, is performed.

Comments

The appearance of the station is clean and functional.

One of the main factors of quality assurance is the regular intercomparison by multipoint calibration between the analysers and an ozone reference (transfer standard) that is traceable to the NIST. The purchase of such an instrument would certainly progress the entire measurements and is therefore very desirable.

Maintenance that is carried out on a case by case basis has its advantage over following a strict schedule due to the fact that there is no unnecessary interruption of the instruments. Since the required experience for such a practice is present we do not recommend any change to this procedure. Even though it differs from the description in the SOP of GAW report No. 97.

4.1.4. Data Handling, Ozone

The present data acquisition facility is installed at the site in the same room as the ozone analysers. It consists of several ADC circuit boards (one for each instrument) to store the data on the computer. Every month the data is reprocessed and recalculated in a spreadsheet file containing the data from all the ozone analysers. For details about data treatment factors see chapter 5.2.
Then the invalid values (according logbook), i.e. data from manual calibration or daily zero / span checks or analytically invalid data, are manually removed from the database. The validated data is averaged to the hourly mean values resulting in a full-data set that remains available for future usage (e.g. study of pollution episodes). In a second step, the full-data set is filtered to achieve a baseline condition data set. This is done using data from the clean air sectors SE - S - SW and, by means of parameters like wind speed, CO or pollution indicators like CFCs. The data sets are stored on a PC and archived monthly on CD (two copies). Once a year they are then sent to the external expert at IFU and are reviewed again. Whenever data are reported, the technique for background data extraction is described.

At the time of the audit, the data acquisition system at the site was in the process of renewal. IFU, Germany, has provided its self-developed TestPoint® application and a 16-bit A/D conversion to Cape Point. The new system will be more user friendly and the data should be easier to survey.

Comments

The procedure of data treatment is well organised and clearly arranged and will be even more improved with the new acquisition system. Any recalculation can easily be traced back to the raw values. The reprocessing of the data is done on a regular monthly interval, i.e. irregularities can be detected early. Reviewing of the final data set by two persons is welcome, since this measure increases the reliability of the data.
The development of a technique for extracting background data is highly regarded and could as well be interesting for other station operators.

The long awaited direct data transfer via modem has been still not possible but is expected to be implemented within the next few months.

4.1.5. Documentation, Ozone

Within the GAW guidelines documents are required. During the audit the documentation was reviewed for availability and usefulness. At Cape Point, a separate, bound logbook is attached to each instrument and is a combination of instrument-, station- and maintenance logbook. The logbook was easy accessible at the site and contained all necessary information about maintenance, changes, events and special investigations. A station specific system operating procedure (SOP) for maintenance was not available.

Comment

The documentation of the ozone measurement meets all the requirements of the GAW guidelines. As pointed out already during the last audit, it would be very desirable to have a practice orientated SOP for maintenance and operation, as a preventive action to avoid loss of accumulated knowledge due to personnel changes.

4.2. Carbon Monoxide (in situ)

4.2.1. Air Inlet System for CO

The air inlet system for the CO measurements is mounted at the 30 meter level of the mast. It consists of a small, inverse plastic funnel which shields a 1/4" stainless steel tube from rain. The around 40 m long tube leads down along the tower through a hole in the roof to the air-conditioned laboratory building where the RGA-3 CO analyser is installed. The ambient air is sucked through that outside line by a pump (12 l / min) and then pre-treated in a two stage freezing unit (1.: $-4°C$ and 2.: $-35°C$) to remove water vapour. A small portion of the stream (50 ml/min) is split off flushing the 1ml sample loop. The residence time of the ambient air in the inlet line lies around 3 seconds.

Comments

The inlet system installed is adequate for analysing CO concerning construction materials as well as residence time.

4.2.2. Instrumentation, CO Analyser

The in situ CO analyser, an RGA-3 GC-system, is installed in the spacious air-conditioned room (temperature raise of about 4°C on a sunny hot day was observed) of the laboratory building.

Instrumental details for the carbon monoxide analyser on site are listed in table 3.

Table 3: Field CO analyser

instrument	Trace Analytical GC
model	RGA-3 gas chromatograph
at Cape Point	since December 1989
method	GC / HgO Detector

interval of sample injection	12 min
loop	1 ml, flushed at 50 ml/min
column	analytical column: Mole sieve 5A 60/80
carrier gas	synthetic air - Mole sieve - Hopcalite - Sofnocat - GC, 20 ml/min
operating temperatures	Detector: 202 °C, Column: 97 °C
analog output	0-1 V
calibration interval	working standard analysis every 3 hours
instrument's specials	a few seconds before injection, the flow through the loop is stopped (solenoid valve) to equalise the pressure inside the loop to ambient pressure

The zero air unit consists of a synthetic air cylinder and of three filter cartridges comprising molecular sieve, Hopcalite and sofnocat respectively. Four times a year it is used to check the analyser's zero readings.

Comments

The gas chromatography technique followed by mercury reduction detection, as operated at Cape Point, is a widely used method for background air measurements. Applied with care it is characterised by excellent specificity, very low detection limits and high precision (WMO-GAW report No. 98). However, attention should be given to the relation between detector signal and concentration (non-linearity) of the actual configuration. The analyser RGA-3, although in operation for around 10 years, is in good condition.

4.2.3. Gas Standards, CO

The following gas standards are used at the site for verification of the measurements.

Table 4: Station CO cylinders

	Gas cylinders at the site	filling	Conc.
1	working standard, Air Products, calibrated against IFU primary standard	synthetic air	64 ppb
2	IFU primary standard, reference, traceable to CMDL	synthetic air	61.3 ppb
3	certified CMDL standards, ID 2907	synthetic air	45.0 ppb
4	certified CMDL standards, ID 2929	synthetic air	69.4 ppb
5	for linearity check, using a dilution system	synthetic air	10 ppm

Ordered standards (to date of audit not received yet):

5 - 7	Scott-Marrin, Inc. Standard, not CMDL certified	synthetic air	40 / 80 / 150 ppb

While the working standard is analysed once every three hours, once daily one of the two certified CMDL station standards is injected in addition. These two standards have only been used for stability check purposes, over the past two years. The reason why they have not been taken into account for calibration, and thus used to calculate a multipoint calibration function, is because the measured values (relative to the working standard) and those given on the CMDL certificate have deviated. According to the station manager, this has always been a matter of concern so they had ordered (but not received yet) three Scott-Marrin, Inc. Standards (not certified by CMDL).

All CO measurement values at Cape Point are determined relative to the value of the working standard, which in turn, is compared to the station primary standard supplied by IFU. Standards from IFU are, in principle, traceable to the CMDL scale.

Comments

The very frequent checks of the system with a working standard and the daily stability check with a CMDL standard, both within the relevant range of the site, validate the measurements. All measurement values are based on the IFU standards but the traceability to CMDL standards is still guaranteed.

4.2.4. Operation and Maintenance, CO

Most of the maintenance works for the RGA-3 CO analyser are performed on a case by case basis, i.e. exchanging the lamp, resetting the electronic baseline and baking out of the analytical column at 220°C when the baseline becomes noisy.

Twice a week, the station operators inspect the CO measurements for a quick check of general operation of the analysers. This includes checking of RGA-3 test points and controlling some chromatograms.

The system is calibrated with a CO working standard (64ppb) which is injected alternatingly with ambient air. For a more detailed description of the standard handling see section 4.2.3 Gas Standards. Four times a year, the analyser's zero readings are checked. They are performed as an integral part of multipoint calibration checks, twice annually, utilising a 10 ppm CO standard that is diluted with zero air using flow meters.

Comments

The appearance of the station is clean and functional.

Because of the operators experience with gas chromatography, the maintenance is carried out on a case by case basis. The check of some analyser test points and controlling chromatograms gives the operator enough information about the state of the instrument to determine if maintenance is necessary. When the modem connection is realised finally, this control can be even intensified.

4.2.5. Data Handling, CO

The data acquisition facility consists of a PC with an ADC board and the "APEX" GC control software. Chromatograms are stored until they are recalculated and the data is reviewed. From the results of the working standard, a moving average encompassing three calibrations is run over the whole set of monthly calibrations. The individual value (moving average) from the calibration peak adjacent to the corresponding ambient air peak is used to calculate the ambient air concentration. Chromatogram integration is carried out for peak height. Invalid values (according

logbook), i.e. data from manual calibration or zero checks or analytically invalid data, are manually removed from the database. The validated 12-minute CO values are averaged to the hourly mean values resulting in a full-data set that remains available for future usage (e.g. study of pollution episodes). In a second step, the full-data set is filtered to achieve a baseline condition data set. This is done using data from the clean air sectors SE - S - SW and, by means of parameters like wind speed, O_3 or pollution indicators like CFCs. The data sets are stored on a PC and archived monthly on CD (two copies). Once a year they are then sent to the external expert at IFU and are reviewed again. Whenever data are reported, the technique for background data extraction is described.

Since mid-1997 raw data including chromatograms are being archived on CD on a monthly basis. This makes it possible for chromatograms to be reintegrated in the future. Once a year they are then sent to the external expert at IFU (twinning partner of the Cape Point station) and are reviewed again.

To date no data has been distributed to the GAW WDC for greenhouse gases, Tokyo.

Comments

The procedure of data treatment is well organised and clearly arranged. The procedure of data handling is similar to the ozone measurements. Since mid-1997 raw data including chromatograms are being archived on CD on a monthly basis. This welcomed effort makes it possible for chromatograms to be reintegrated in the future.

The available data should be sent to the WDC for greenhouse gases as soon as calibration queries and quality assurance issues have been settled.

4.2.6. Documentation, CO

The documentation is identical as for the ozone measurements at Cape Point.

Comments

See ozone 4.1.5.

5. Intercomparison of Ozone Instruments

5.1. Experimental Procedure

At the site, the transfer standard (detailed description see Appendix II) was hooked up to power for warming up over the weekend, in deviation from the GAW Report No. 97 which recommends only one hour of warm-up. In the morning, before the intercomparison was started the transfer standard, the PFA tubing connections to the instrument and the instrument itself were conditioned with about 250 ppb ozone for 40 min. During the next few days, three comparison runs between the field instrument and the EMPA transfer standard were performed. In the meantime the inlet system and the station documentation were inspected. Table 5 shows the experimental details and Figure 8 the experimental set up of the audit. In general, no modifications of the ozone analysers which could influence the measurements were made for the intercomparison.

The EMPA acquisition system which was used for the audit consisted of a 16-channel ADC circuit board and a PC with the corresponding software. Hooked up to the analog output of the field instrument and of the transfer standard, the data were collected. The EMPA data acquisition and the site data acquisition system were compared. For data interpretation the EMPA data is used.

Finally, the observed results were discussed in an informal review with the persons involved.

The audit procedure included a direct intercomparison of the TEI 49C-PS transfer standard with the Standard Reference Photometer SRP#15 (NIST UV photometer) before and after the audit in the calibration laboratory at EMPA. The results are shown in the Appendix III.

Table 5: Experimental details, ozone

audit team, WCC	A. Herzog, S. Bugmann
reference:	EMPA: TEI 49C-PS #54509-300 transfer standard
field instruments:	TEI 49 #51594-288 Dasibi 1008RS #4840
ozone source:	EMPA: TEI 49C-PS, internal generator
zero air supply:	EMPA: silica gel - inlet filter 5 μm - metal bellow pump - Purafil (potassium permanganate) - activated charcoal - outlet filter 5 μm
data acquisition system:	EMPA: 16-channel ADC circuit board, software
pressure transducers reading:	reference*: 994.3 hPa TEI 49C-PS: 994 hPa, TEI 49: 997 hPa Dasibi 1008RS: 998 hPa
concentration range	0 - 100 ppb
number of concentrations:	5 + zero air at start and end
approx. concentration levels:	10 / 20 / 30 / 50 / 90 ppb
sequence of concentration:	random
averaging interval per concentration:	10 minutes

number of runs:	TEI 49: 2 x on Sept. 7 and 1 x on Sept. 8, 1998 Dasibi: 1 x on Sept. 8 and 2 x on Sept. 9, 1998
connection between instruments:	approx. 1.2 meter of 1/4" PFA tubing

* pressure transducer reference: station barometer
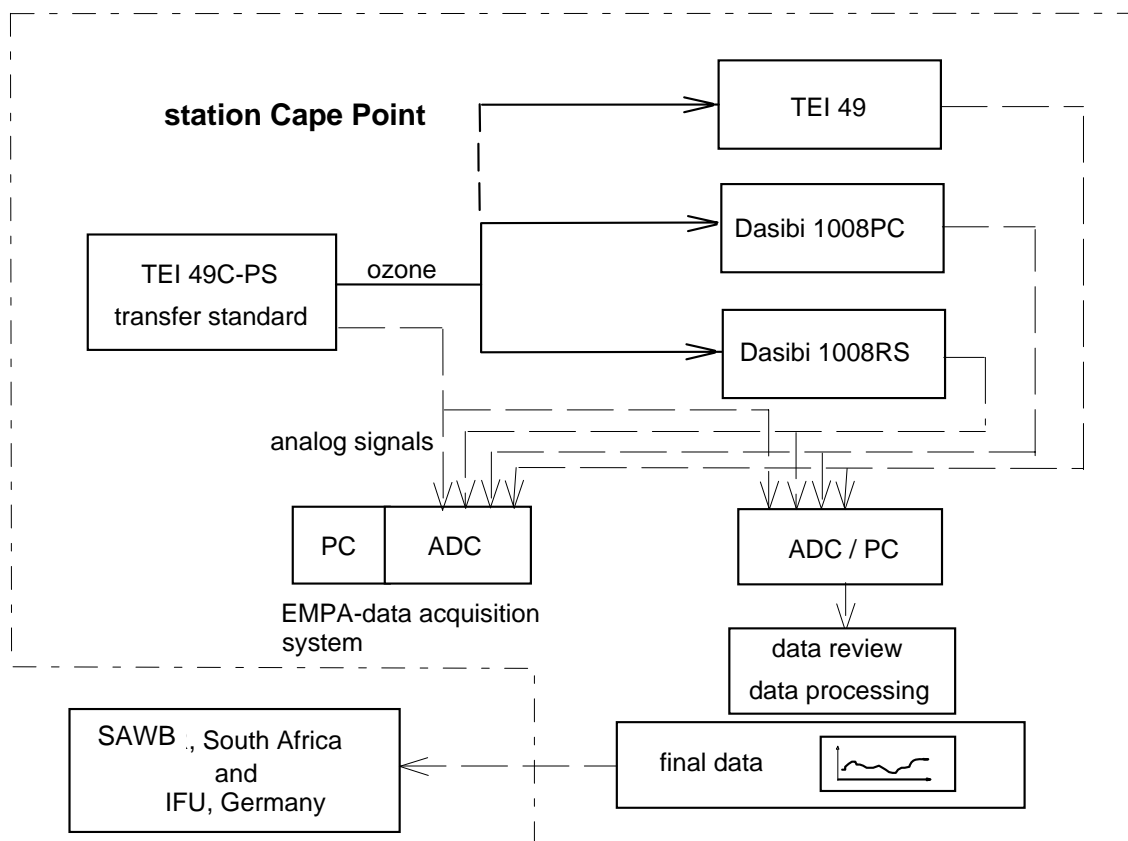
Figure 8: Experimental set up, ozone

5.2. Results

The results comprise the three runs of the intercomparisons between the two field instruments TEI 49 and Dasibi 1008RS and the transfer standard TEI 49C-PS, carried out between September 7/9, 1998.

In the following tables 6-8 and 9-11, the resulting mean values of each ozone concentration and the standard deviations (s_d) of twenty 30-second-means (10min) are presented. For each mean value the differences between the tested instruments and the transfer standard are calculated in ppb and in %. Further, the diagrams show the results of the linear regression analysis of both field instruments compared to the EMPA transfer standard.

The data used for the evaluation were recorded by the EMPA data acquisition system. This raw data was treated according the usual station specific procedure:

Dasibi 1008RS minus determined offset 2.8 ppb (monthly mean from daily zero checks), then the factor 1.053 is applied

TEI 49:   minus determined offset 5.5 ppb (monthly mean from daily zero checks)

Table 6:   1. Intercomparison, TEI 49

| No. | transfer standard | | TEI 49 #288 | | | |
| | TEI 49C-PS conc. | S_d | conc. (-5.5 ppb) | S_d | deviation from reference | |
	ppb	ppb	ppb	ppb	ppb	%
1	0.4	0.25	0.5	0.17	0.0	
2	29.7	0.28	29.9	0.32	0.3	0.9%
3	49.6	0.32	49.6	0.23	0.0	-0.1%
4	9.7	0.17	9.5	0.16	-0.2	-2.3%
5	19.8	0.25	19.6	0.26	-0.3	-1.3%
6	89.4	0.26	89.2	0.35	-0.2	-0.2%
7	0.4	0.16	0.2	0.24	-0.2	

Table 7:   2. Intercomparison, TEI 49

| No. | transfer standard | | TEI 49 #288 | | | |
| | TEI 49C-PS conc. | S_d | conc. (-5.5 ppb) | S_d | deviation from reference | |
	ppb	ppb	ppb	ppb	ppb	%
1	0.4	0.16	0.2	0.24	-0.2	
2	49.6	0.16	49.5	0.21	-0.1	-0.1%
3	19.6	0.32	19.4	0.11	-0.3	-1.3%
4	89.3	0.22	89.0	0.24	-0.3	-0.4%
5	29.5	0.17	29.6	0.23	0.0	0.1%
6	9.8	0.24	9.6	0.17	-0.2	-2.5%
7	0.2	0.20	0.1	0.26	-0.1	

Table 8:   3. Intercomparison, TEI 49

| No. | transfer standard | | TEI 49 #288 | | | |
| | TEI 49C-PS conc. | S_d | conc. (-5.5 ppb) | S_d | deviation from reference | |
	ppb	ppb	ppb	ppb	ppb	%
1	0.7	0.26	0.2	0.26	-0.4	
2	89.8	0.46	89.0	0.38	-0.7	-0.8%
3	50.0	0.30	49.4	0.33	-0.5	-1.1%
4	19.9	0.38	19.3	0.23	-0.6	-2.8%
5	10.0	0.25	9.5	0.32	-0.4	-4.2%
6	29.8	0.38	29.4	0.26	-0.4	-1.4%
7	0.6	0.20	-0.1	0.31	-0.6	

Table 9:　　1. Intercomparison, Dasibi 1008RS

No.	transfer standard		Dasibi 1008RS #4840			
	TEI 49C-PS conc.	S_d	conc. (-2.8 ppb)	S_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.3	0.24	-0.5	0.32	-0.8	
2	49.7	0.21	47.8	0.46	-1.9	-3.8%
3	19.8	0.17	18.8	0.44	-1.0	-4.9%
4	89.9	0.26	87.2	0.48	-2.7	-3.0%
5	29.9	0.18	28.5	0.53	-1.4	-4.6%
6	9.9	0.24	9.3	0.33	-0.6	-6.3%
7	0.3	0.25	-0.6	0.47	-0.9	

Table 10:　2. Intercomparison, Dasibi 1008RS

No.	transfer standard		Dasibi 1008RS #4840			
	TEI 49C-PS conc.	S_d	conc. (-2.8 ppb)	S_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.5	0.39	-0.7	0.34		
2	29.9	0.20	28.4	0.41	-1.5	-5.0%
3	89.8	0.24	85.6	0.60	-4.2	-4.7%
4	49.9	0.39	48.0	0.40	-1.9	-3.9%
5	10.0	0.40	9.1	0.51	-0.9	-8.9%
6	20.0	0.21	18.7	0.41	-1.2	-6.2%
7	0.5	0.16	-0.7	0.44	-1.1	

Table 11:　3. Intercomparison, Dasibi 1008RS

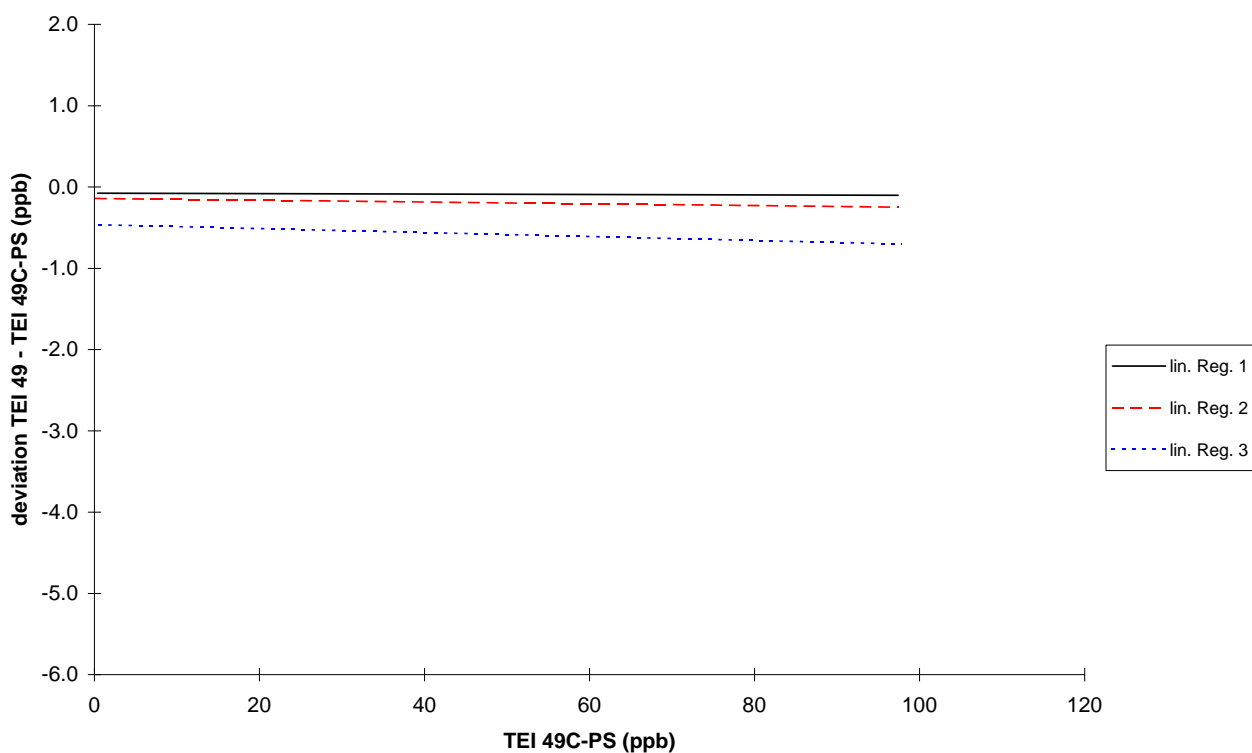| No.	transfer standard		Dasibi 1008RS #4840			
	TEI 49C-PS conc.	S_d	conc. (-2.8 ppb)	S_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.7	0.12	-1.0	0.47	-1.6	
2	19.9	0.14	18.6	0.29	-1.3	-6.4%
3	49.8	0.18	47.5	0.29	-2.3	-4.6%
4	10.0	0.18	8.9	0.38	-1.1	-11.2%
5	89.9	0.20	86.4	0.51	-3.6	-4.0%
6	30.0	0.14	28.4	0.37	-1.6	-5.2%
7	0.3	0.21	-0.7	0.27	-1.0	

Figure 9: Individual linear regressions of intercomparisons 1 to 3, TEI 49
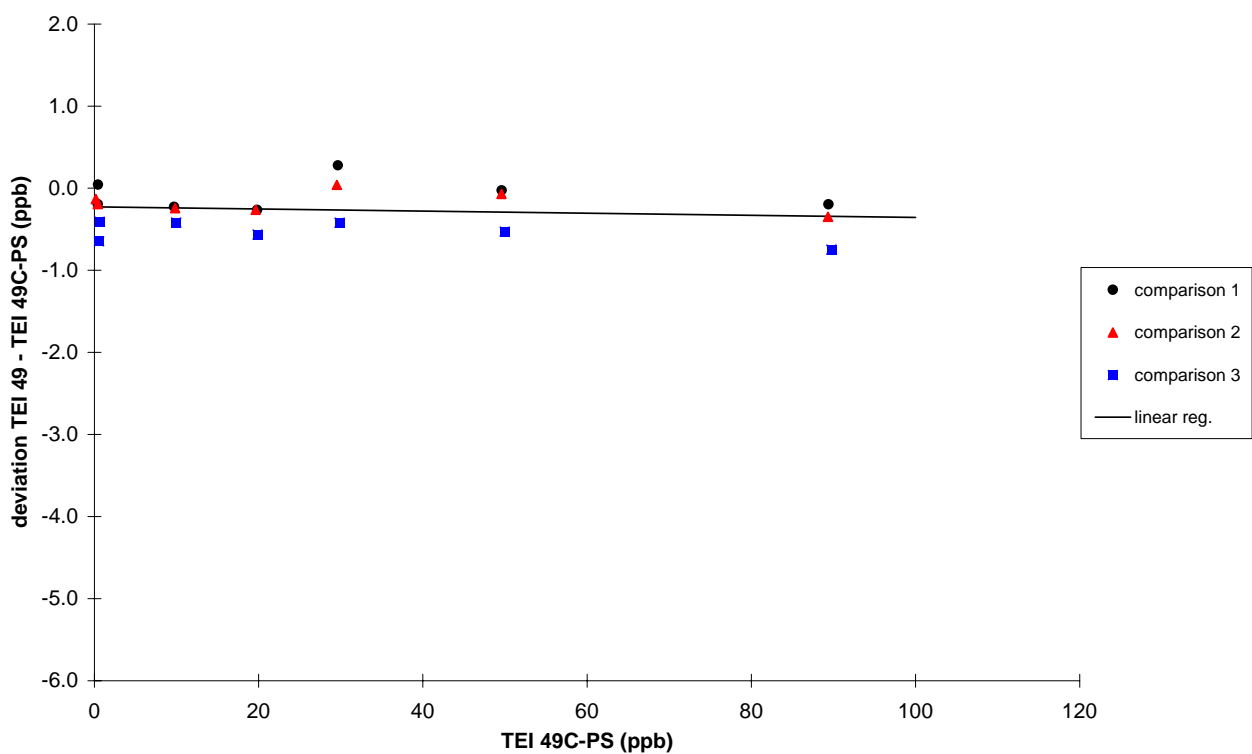

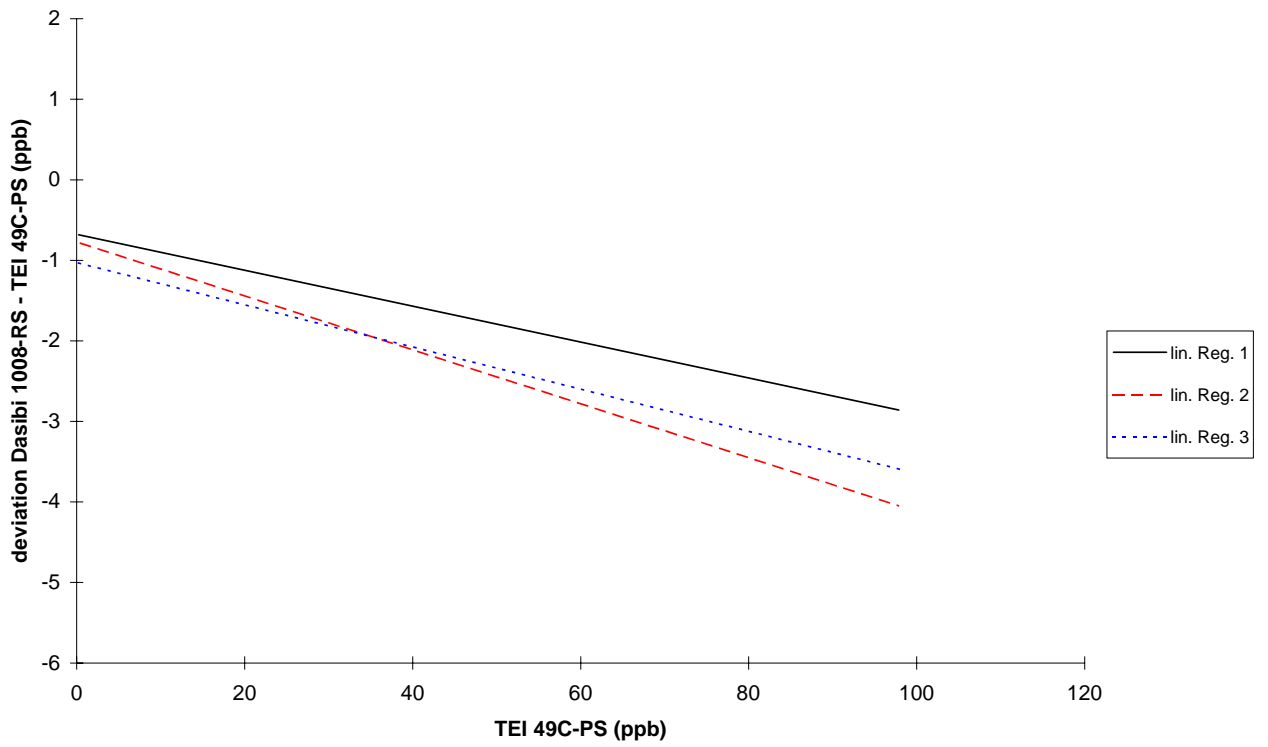Figure 10: Mean linear regression of intercomparisons 1 to 3, TEI 49

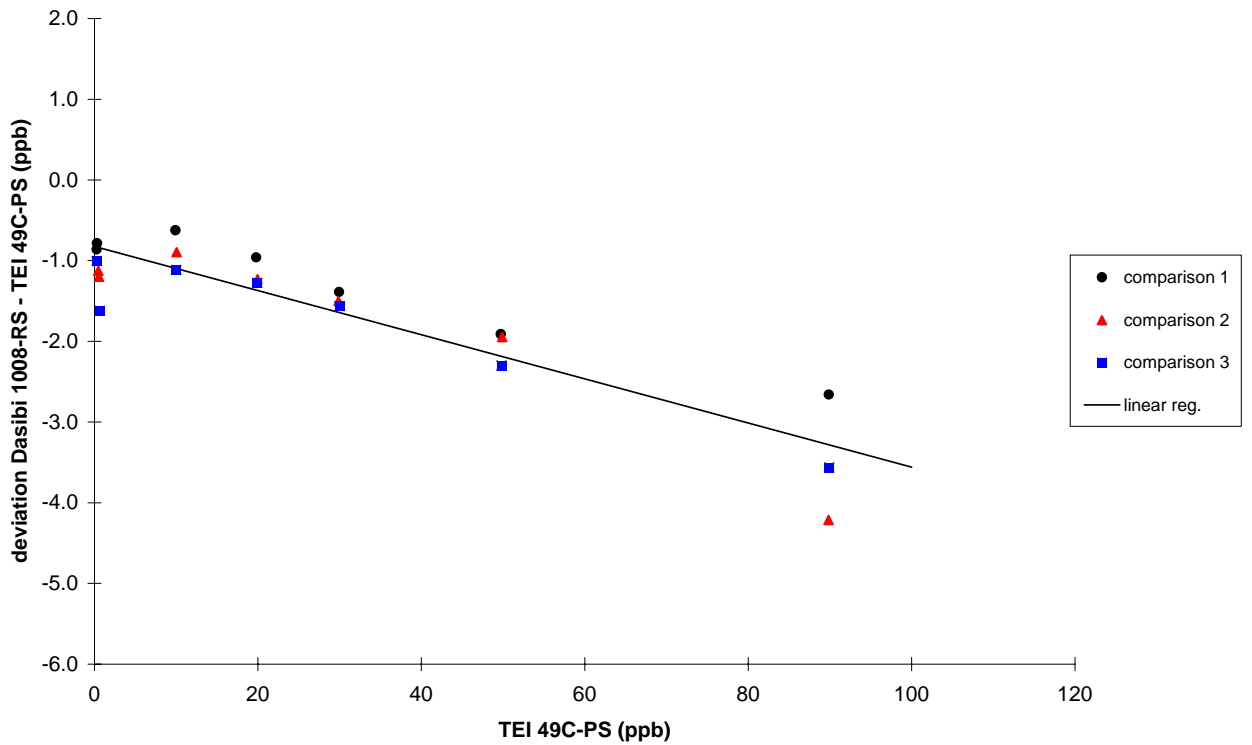Figure 11: Individual linear regressions of intercomparisons 1 to 3, Dasibi 1008RS

Figure 12: Mean linear regression of intercomparisons 1 to 3, Dasibi 1008RS

From the intercomparisons of the Thermo Environmental Instrument TEI 49 #288 and the Dasibi 1008RS #4840 with the TEI 49C-PS transfer standard from EMPA the following equations (for the range of 5-100 ppb ozone) result:

-TEI 49:

$$TEI\ 49 = 0.999 \times TEI\ 49C\text{-}PS - 0.2\ ppb$$

TEI 49 = O_3 mixing ratio in ppb, determined for TEI 49 #51594-288
TEI 49C-PS = O_3 mixing ratio in ppb, related to TEI 49C-PS #54509-300

Standard deviation of: - slope s_m 0.0018 (f = 3) f=degree of freedom
                        - offset S_b in ppb   0.08   (f = 3)
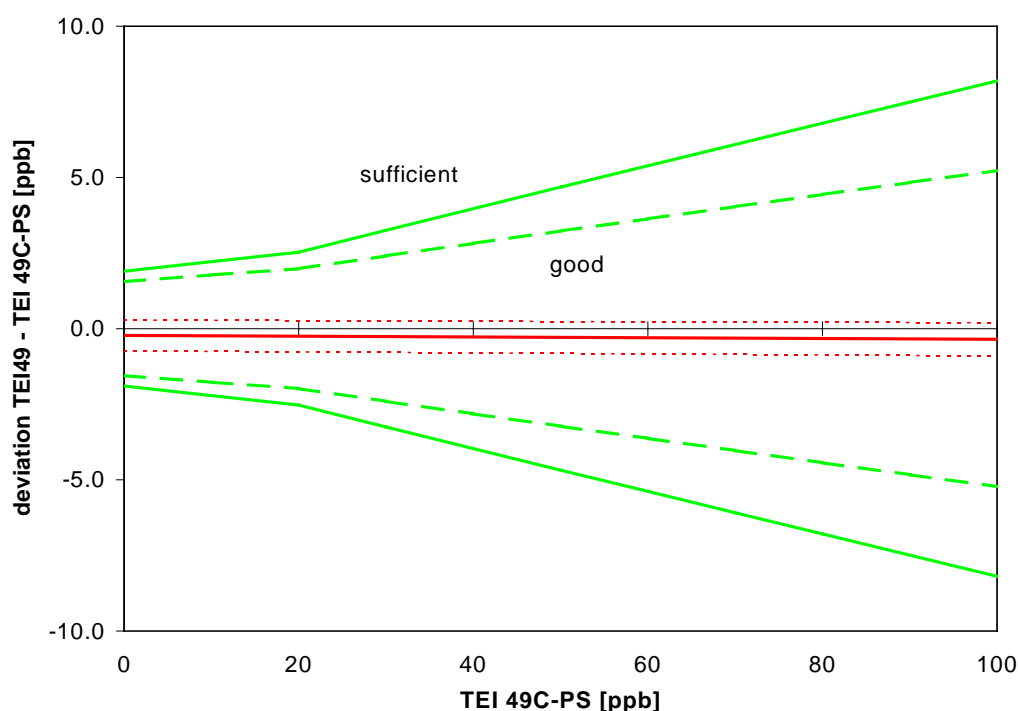   - residuals in ppb   0.14   (f = 19)

Figure 13: Intercomparison of ozone instrument TEI 49 (linear regression with prediction interval 95%)

-Dasibi 1008RS:

$$Dasibi\ 1008RS = 0.973 \times TEI\ 49C\text{-}PS - 0.8\ ppb$$

Dasibi 1008RS = O_3 mixing ratio in ppb, determined for Dasibi 1008RS #4840
TEI 49C-PS = O_3 mixing ratio in ppb, related to TEI 49C-PS #54509-300

Standard deviation of: - slope s_m 0.0029 (f = 3) f=degree of freedom
                        - offset S_b in ppb   0.12   (f = 3)
                        - residuals in ppb   0.32   (f = 19)

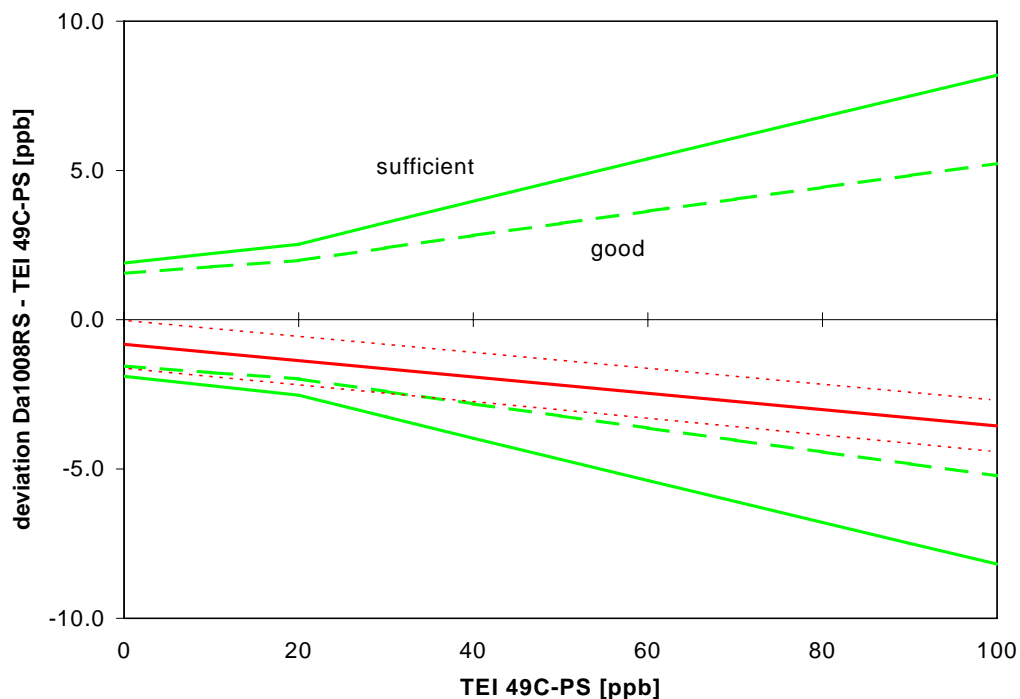Figure 14: Intercomparison of ozone instrument Dasibi 1008RS (linear regression with prediction interval 95%)

Comments

The ozone concentration observed at Cape Point (1997) usually ranged between 12 and 32 ppb (5- and 95-percentile of hourly mean values). The basic and the backup instruments fulfil the assessment criteria as "good" over the tested and relevant range up to 100 ppb (figures 13 and 14).

6. Intercomparison of in situ Carbon Monoxide Analyser

6.1. Experimental Procedure

No official WMO Standard Operation Procedure (SOP) has been established for CO measurements until now. For this reason, the "SOP for performance auditing ozone analysers at global and regional WMO-GAW sites" (WMO-GAW Report No 97), was adapted for CO accordingly.

At the site the two CMDL CO transfer standards (100 and 200 ppb CO) and the two self-pressurised canisters (50, 150 ppb CO) were stored in the same room as the CO measurement system to temper over the weekend. The cylinders were connected to the measurement system as can be seen in figure 15. The pressure regulators and stainless steel tubings were flushed extensively and leak checked (no drop of pressure for half an hour with main cylinder valve closed). Between 6. – 11. September, each transfer standard was injected and analysed between 3 to 38 times. The automated analysis procedure with an injection every 12 minutes was performed in an alternating fashion: station working standard – EMPA transfer standard - station working standard. In general, no modification of the carbon monoxide RGA-3 gas chromatograph was made for the intercomparison. The chromatograms were acquired by the station "APEX GC control" software. The data (mean values and standard deviations) was processed in the conventional way, similar to that used for ambient calculations and delivered to the WCC.

Finally, the observed results were discussed in an informal review with the person involved.

The audit procedure included a direct intercomparison of the two CMDL transfer standards and the two self-pressurised canisters, respectively, with the CMDL Laboratory Standard before and after the audit in the WCC calibration laboratory at EMPA.

Table 12:   Experimental details, carbon monoxide

|	
audit team, WCC	A. Herzog, S. Bugmann
EMPA transfer standards:	CMDL transfer standards (ppb): FAO1469; FAO1467 and two self-pressurised canisters
field instrument:	RGA-3
zero air supply:	station: synthetic air – molecular sieve – Hopcalite – sofnocat
data acquisition system:	ADC Board, APEX GC control software
surrounding conditions:	p: 995 hPa $\pm$ 2 hPa and T_{indoor}: approx. 22°C
number of concentrations:	5
approx. concentration levels:	50 / 100 / 150 / 200 ppb
number of injection per concentration:	3 to 38 times
sequence	alternatingly: working standard – EMPA standard
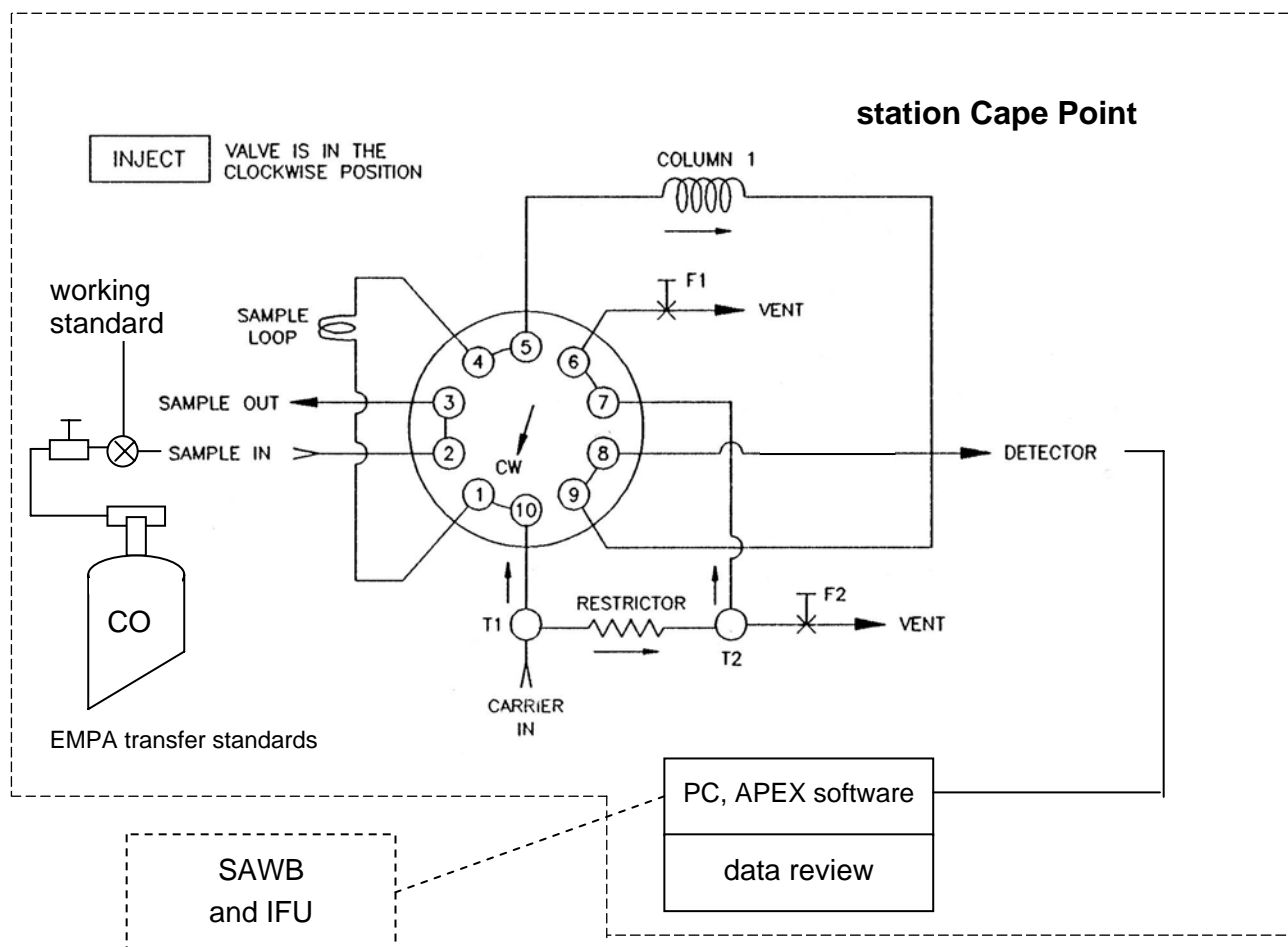
Figure 15: Experimental set up, carbon monoxide

6.2. Results

The results consist of the intercomparisons, carried out between 6. – 11. September 1998, between the field instrument RGA-3 and four CMDL transfer standards of the EMPA. The values from the RGA-3 field instrument had been delivered by the station operator and are based on the primary standard of IFU, Germany.

In the following table the certified mixing ratio (first column) and the resulting mean values of each carbon monoxide concentration including standard deviations are presented. For each mean value the difference between the analysis result (RGA-3) and the certificate of the cylinders is calculated in ppb and in %. Further, figures 16 to 18 show the results of the regression analysis (polynomial curve, 2nd order) of the field instrument compared to the EMPA / CMDL transfer standards.

Table 13:   Intercomparisons, CO

No.	EMPA transfer standards (CMDL)	RGA-3				
	conc.	conc.	s$_d$	No. of	deviation from reference	
	ppb	ppb	ppb	injections	ppb	%
1	44.3	51.7	0.1	11	7.4	16.7
2	99.9	98.4	0.2	32	-2.3	-2.3
3	144.4	136.5	0.1	3	-7.9	-5.5
4	202.1	179.8	0.2	15	-22.3	-11.0

No.	station cylinders (CMDL standards)	RGA-3				
	conc.	conc.	s$_d$	No. of	deviation from reference	
	ppb	ppb	ppb	injections	ppb	%
1	45.0	49.5	0.1	38	4.5	10.0
2	69.4	71.8	0.1	31	2.4	3.5

The summary of the CO comparisons (for the CO range 40 to 210 ppb) of the RGA-3 CO analyser with the EMPA transfer standards is the following polynomial equation:

$$RGA\text{-}3 = -0.00038 \times (EMPA / CMDL)^2 + 0.91 \times EMPA / CMDL + 11.8 \text{ ppb}$$

RGA-3 = CO mixing ratio in ppb, determined for RGA-3 presently at the site
EMPA / CMDL= CO mixing ratio in ppb from the transfer standards of the WCC based on the CMDL scale

It has to be clearly emphasised that the polynomial equation is valid only for the examined range of 40 to 210 ppb CO. However, before applying the function above to the ambient air data, some open points need to be clarified.

1.) The CO (RGA-3 gas chromatograph) results of the intercomparison (figure 17) deviate quite substantially from the conventional true values of the transfer standards by EMPA. Partly, this deviation can be explained by the applied calibration procedure of the station (performing a single point of the RGA-3 system and referring to the IFU scale). However, another possibility that should be considered is that a standard cylinder could have altered with the time.

2.) The annual CO concentration observed to Cape Point typically range from 40 to 70 ppb. However, that relevant range was only covered by two EMPA / CMDL standards (44.3 and 99.9 ppb CO). Thus the polynomial function can be essentially determined by just one of this two data points (see point 1). An outcome of this is that for a next exercise, the WCC should offer additional standard gases considering the station relevant CO range of Cape Point.
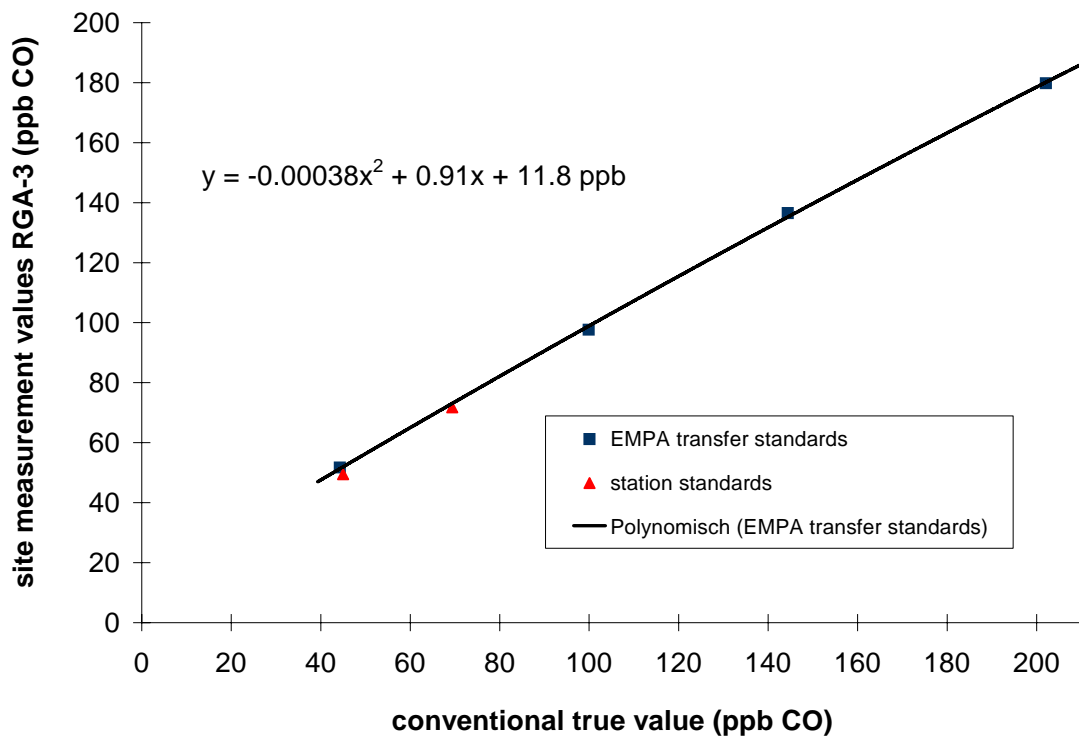
Figure 16: Polynomial curve between RGA-3 and the transfer standards (conventional true value)
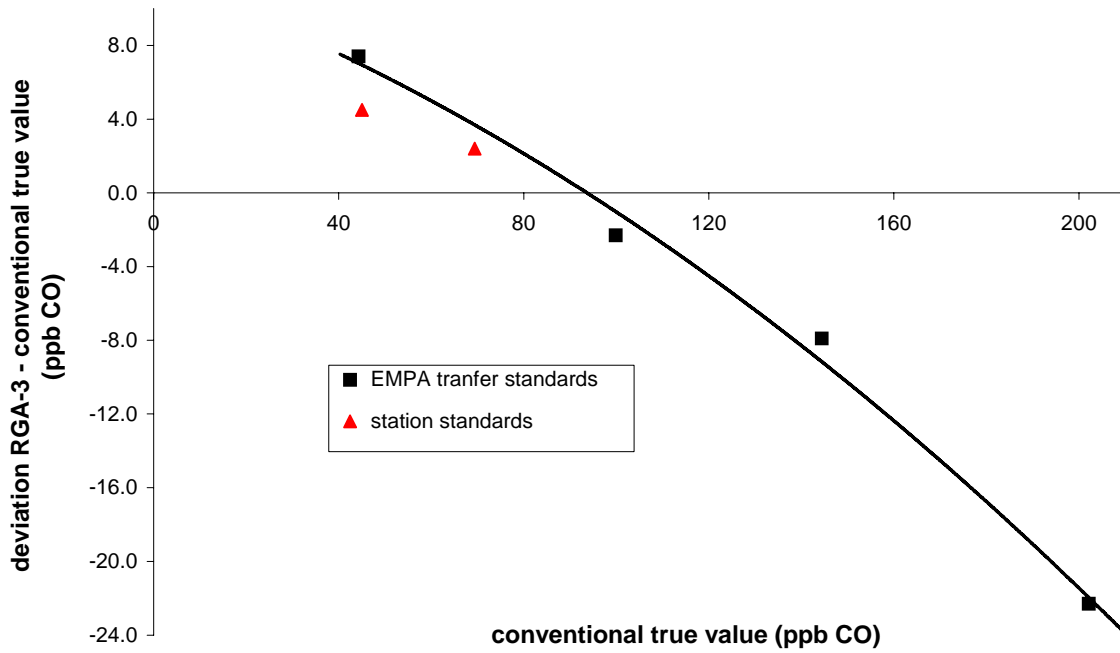

Figure 17: Deviations (ppb) between RGA-3 and the transfer standards (conventional true value)

Figures 16 and 17 show the absolute differences (ppb) between RGA-3 and the transfer standards (conventional true values). The line is the determined polynomial curve (not forced through zero) that is exclusively valid for the range of 40 to 210 ppb CO. The function is representing the best fit for the four EMPA / CMDL standards. Any mixing ratio lower than 40 ppb or higher 210 ppb would require another function to calculate its value. In both graphs the results of the two station standards of CMDL are added. As discussed, in section 4.2.3. Gas Standards, these two standards have been used over the past two years but not been considered for calculating a calibration function.
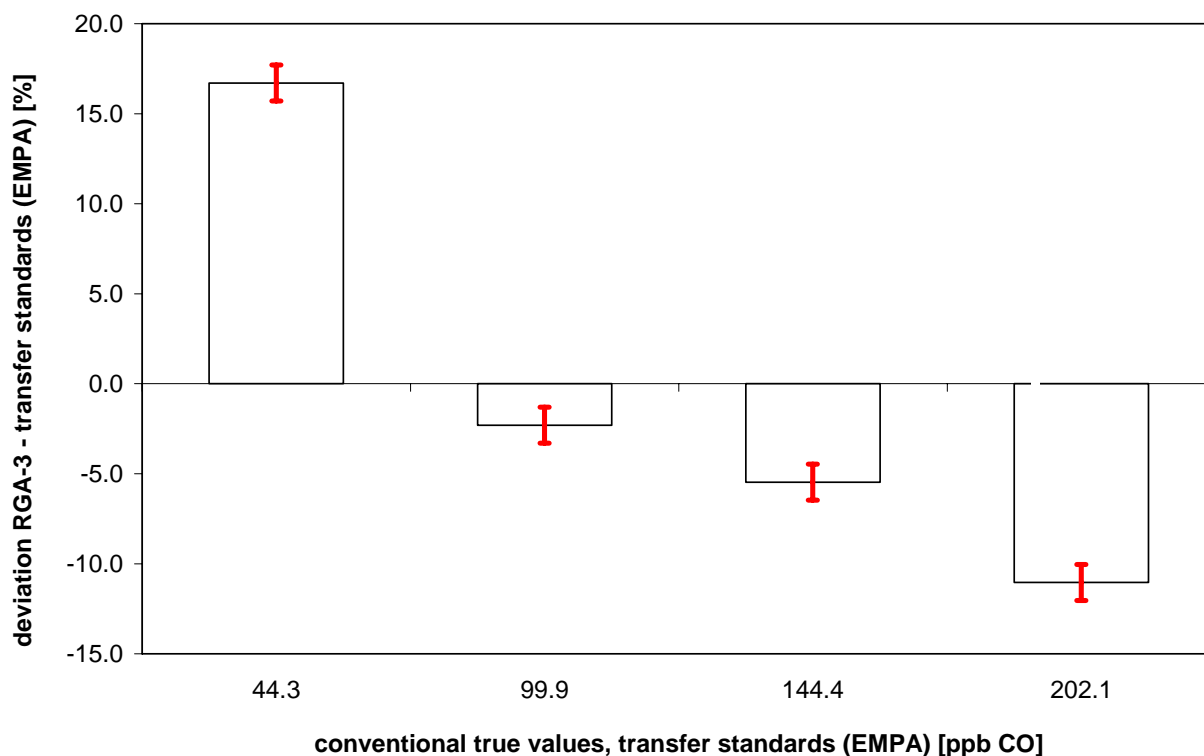

Figure 18: Differences (%) between the RGA-3 and the transfer standard (the red error bars show the given uncertainty of the EMPA / CMDL gas cylinders)

Comment

The CO (RGA-3 gas chromatograph) results of the site deviate quite substantially from the conventional true values of the transfer standards by EMPA. Partly, this deviation can be explained by the applied calibration procedure of the station (performing a single point of the RGA-3 system and referring to the IFU scale). However, another possibility that should be considered is that a standard cylinder could have altered. As a consequence of the noted discrepancy between the EMPA transfer standards and the station standards (all of them are CMDL certified), EMPA will follow up the findings and inform the station operators. Thus, for the moment we do not recommend any data adjustment. For the next audit exercise, it is planned to provide more CO transfer standards in the low ppb range in order for a better coverage of the station's relevant range of CO.

Appendix Ozone

I Results, Intercomparison Dasibi 1008PC

In the course of the intercomparisons of the actual ozone analysers at Cape Point, an intercomparison of the former basic instrument, Dasibi 1008PC #4243, was additionally performed in parallel. The experimental procedure was exactly the same as for the other analysers and is described in chapter 5.1. Some technical data is listed in table 14. The results are shown below in table 15 to 17. Between the first and the second intercomparison the two quartz windows of the cells were replaced by new ones. This modification had no effect on the ozone measurements but the water vapour interference was reduced dramatically. Changing from wet to dry air, using the new quartz windows, a steady state is reached within an hour. With the old quartz windows, several hours of stabilisation time were necessary.

Table 14: Former basic ozone instrument

type	Dasibi 1008PC#4243
method	UV absorption
usage	air intake investigation, 30 m mast
at Cape Point	since 1985
range	0-1000 ppb
analog output	0-1 V
electronic offset	0 (units)
electronic coefficient	308 (absorption coeff.)

Table 15:   1. Intercomparison, Dasibi 1008PC

No.	TE 49C-PS		Dasibi 1008PC#4243			
	conc.	S_d	conc.	S_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.7	0.12	-0.3	0.18	-1.0	
2	19.9	0.14	18.7	0.41	-1.2	-6.1%
3	49.8	0.18	47.4	0.28	-2.4	-4.8%
4	10.0	0.18	8.5	0.37	-1.5	-14.5%
5	89.9	0.20	87.2	0.37	-2.7	-3.0%
6	30.0	0.14	28.1	0.41	-1.9	-6.3%
7	0.3	0.21	-0.4	0.19	-0.7	

Table 16: 2. Intercomparison, Dasibi 1008PC

No.	TE 49C-PS		Dasibi 1008PC#4243			
	conc.	S_d	conc.	S_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.2	0.20	-0.2	0.40		
2	50.0	0.16	47.9	0.37	-2.1	-4.2%
3	10.0	0.16	9.0	0.19	-1.0	-9.8%
4	30.0	0.14	27.7	0.46	-2.3	-7.6%
5	89.9	0.18	87.4	0.40	-2.5	-2.8%
6	20.1	0.22	18.6	0.09	-1.5	-7.6%
7	0.3	0.17	-0.6	0.34	-0.9	

Table 17: 3. Intercomparison, Dasibi 1008PC

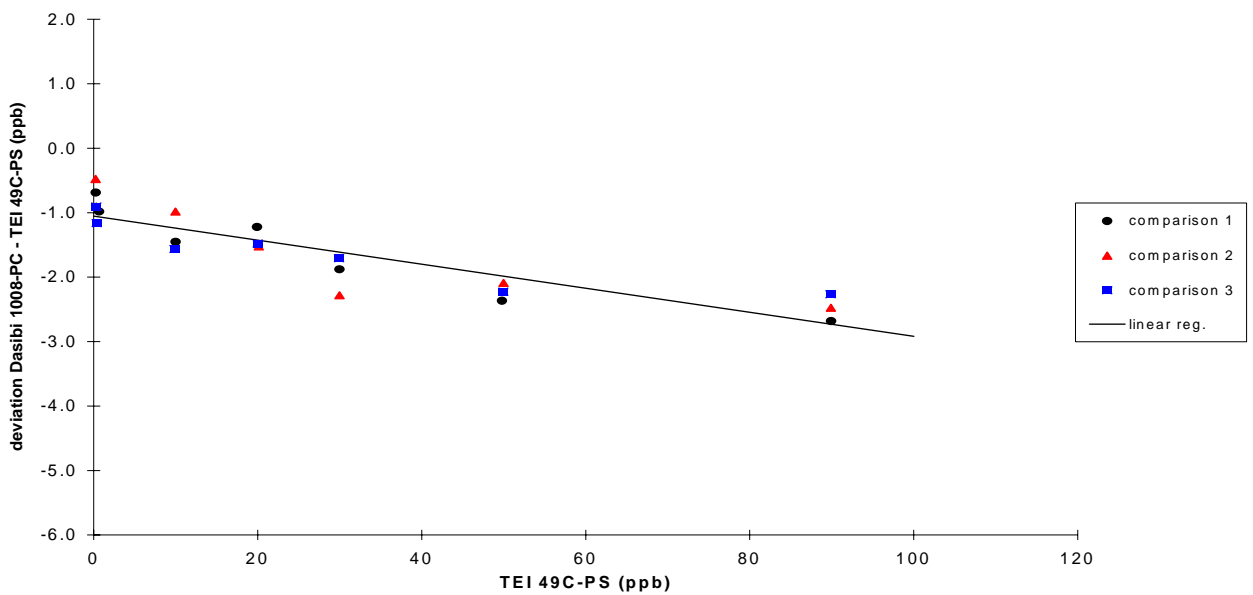| No.	TE 49C-PS		Dasibi 1008PC#4243			
	conc.	S_d	conc.	S_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.3	0.17	-0.6	0.34	-0.9	
2	9.8	0.19	8.3	0.52	-1.6	-15.9%
3	29.9	0.41	28.2	0.33	-1.7	-5.7%
4	89.8	0.74	87.6	0.60	-2.3	-2.5%
5	49.9	0.18	47.7	0.22	-2.2	-4.5%
6	20.0	0.16	18.5	0.37	-1.5	-7.4%
7	0.4	0.13	-0.8	0.11	-1.2	

Figure 19: Mean linear regression of intercomparisons 1 to 3 , Dasibi 1008PC

From the intercomparisons of the Dasibi 1008PC #4243 field instrument with the TEI 49C-PS transfer standard from EMPA the resulting linear regression (for the range of 0-100 ppb ozone) is:

Dasibi 1008PC   = 0.981 x TEI 49C-PS - 1.05

Dasibi 1008PC = O_3 mixing ratio in ppb, determined for Dasibi 1008PC #4243
TEI 49C-PS = O_3 mixing ratio in ppb, related to TEI 49C-PS #54509-300

Standard deviation of: - slope s_m 0.0023 (f = 3) f=degree of freedom
                                     - offset S_b in ppb   0.09   (f = 3)
                                     - residuals in ppb   0.32   (f = 19)

II EMPA Transfer Standard TEI 49C-PS

The Model 49C-PS is based on the principle that ozone molecules absorb UV light at a wavelength of 254 nm. The degree to which the UV light is absorbed is directly related to the concentration as described by the Lambert-Beer Law.

Zero air is supplied to the Model 49C-PS through the zero air bulkhead and is split into two gas streams, as shown in Figure 20. One gas stream flows through a pressure regulator to the reference solenoid valve to become the reference gas. The second zero air stream flows through a pressure regulator, ozonator, manifold and the sample solenoid valve to become the sample gas. Ozone from the manifold is delivered to the ozone bulkhead. The solenoid valves alternate the reference and sample gas streams between cells A and B every 10 seconds. When cell A contains reference gas, cell B contains sample gas and vice versa.

The UV light intensities of each cell are measured by detectors A and B. When the solenoid valves switch the reference and sample gas streams to opposite cells, the light intensities are ignored for several seconds to allow the cells to be flushed. The Model 49C-PS calculates the ozone concentration for each cell and outputs the average concentration.
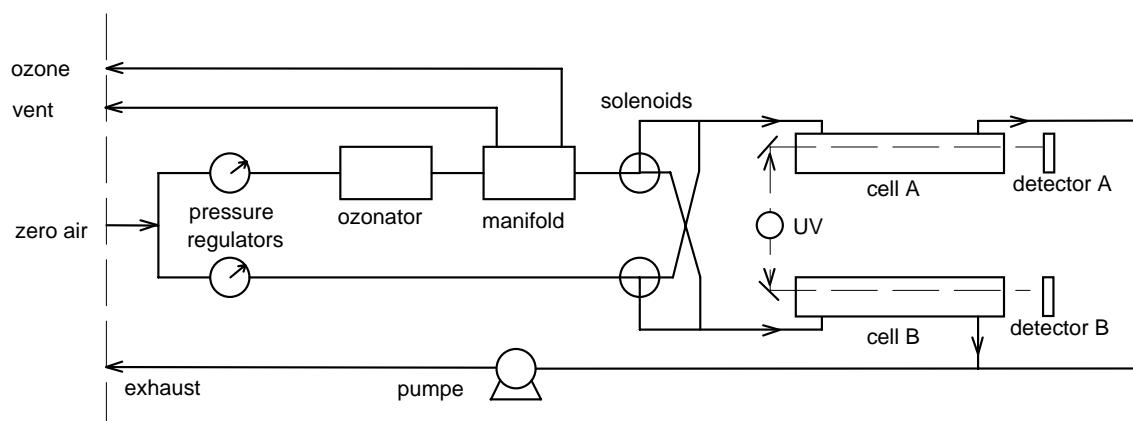

Figure 20: Flow schematic of TEI 49C-PS

III Stability of the Transfer Standard TEI 49C-PS

To exclude errors which might occur through transportation of the transfer standard, the TEI 49C-PS #54509-300 has to be compared with the SRP#15 before and after the field audit.

The procedure and the instruments set up of this intercomparison in the calibration laboratory at EMPA are summarised in Table 18 and Figure 21.

Table 18: Intercomparison procedure SRP - TEI 49C-PS

|	
pressure transducer:	zero and span check (calibrated barometer) at start and end of procedure
concentration range:	0 - 200 ppb
number of concentrations:	5 + zero air at start and end
approx. concentration levels:	30 / 60 / 90 / 125 / 185 ppb
sequence of concentration:	random
averaging interval per concentration:	5 minutes
number of runs:	3 before and 3 after audit
zero air supply:	Pressurised air - zero air generator (CO catalyst, Purafil, charcoal)
ozone generator:	SRP's internal generator
data acquisition system:	SRP's ADC and acquisition
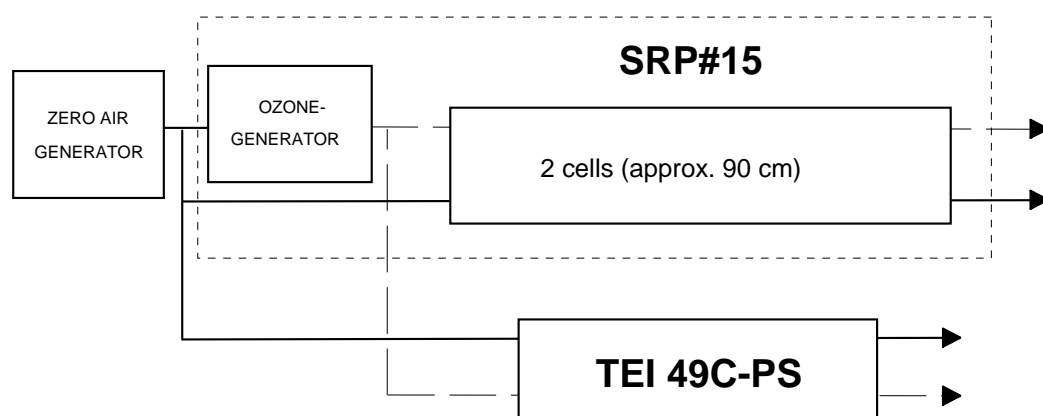
Figure 21: Instrument set up SRP - TEI 49C-PS

The stability of the transfer standard is thoroughly examined with respect to the uncertainties of the different components (systematic error and precision). For the GAW transfer standard of the EMPA-WCC (TEI 49C-PS) the assessment criteria, taking into account the uncertainty of the SRP, are defined to $\pm$ (1 ppb + 0.6%).

Figures 22 and 23 show the resulting linear regression and the corresponding 95% precision interval for the comparisons of TEI 49C-PS vs. SRP#15. Clearly, the results show that the EMPA transfer standard fulfilled the recommended criterias for the period of the audit, including transportation.
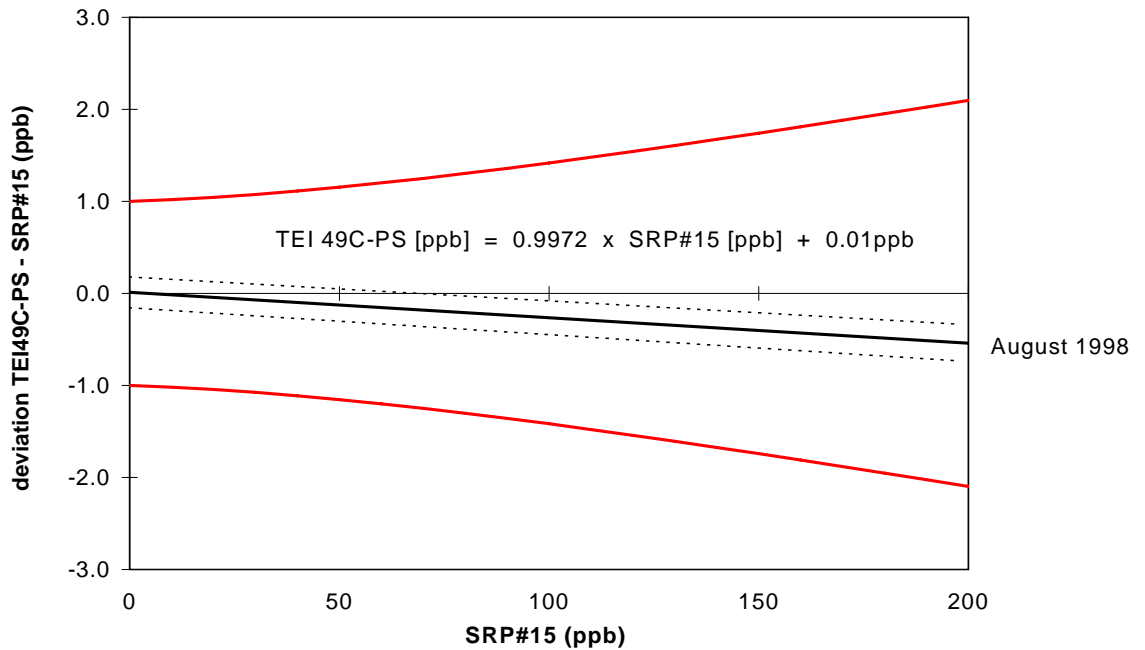

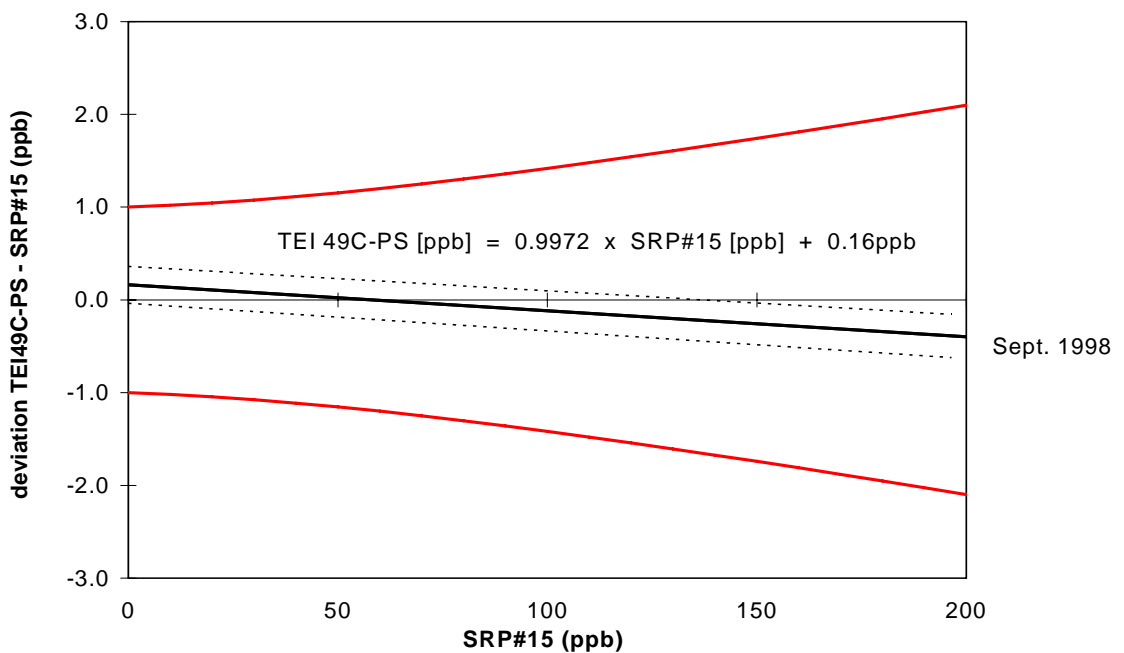Figure 22: Transfer standard pre-audit check, ozone

Figure 23: Transfer standard post-audit check, ozone

Appendix Carbon Monoxide

WCC CO Standards

The carbon monoxide reference scale created by the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) is used to quantify measurements of CO in the atmosphere, calibrate standards of other laboratories and to otherwise provide reference gases to the community measuring atmospheric CO. This CO reference scale developed at CMDL was designated by WMO as the reference within the GAW programme. The absolute accuracy of the NOAA/CMDL CO scale has not been rigorously determined, but based on the uncertainties of the gravimetric and analytical procedures, and comparisons to the NIST CO scale, the NOAA/CMDL scale is probably accurate to within 3%. At the WCC we use the following standards:

Table 19: CO Standards at the WCC

Standard (Gas Cylinders)	CO	Cylinder
CMDL Laboratory Standard (basis for WCC)	44.0 ± 1.0 nmole/mole	CA03209
CMDL Laboratory Standard (")	97.6 ± 1.0 nmole/mole	CA02803
CMDL Laboratory Standard (")	144.3 ± 1.4 nmole/mole	CA03295
CMDL Laboratory Standard (")	189.3 ± 1.9 nmole/mole	CA02859
CMDL Laboratory Standard (")	287.5 ± 8.6 nmole/mole	CA02854
CMDL Transfer Standard (6 l cylinder)	99.9 ± 1.0 nmole/mole	FAO1469
CMDL Transfer Standard (6 l cylinder)	202.1 ± 2.0 nmole/mole	FAO1467
CMDL Transfer Standard (6 l cylinder)	297.8 ± 9.1 nmole/mole	FAO1477

EMPA Transfer Standard (Rasmussen canister 1.8 l, electropolished stainless steel)	44.3 ± 1.0 nmole/mole	canister #1
EMPA Transfer Standard (Rasmussen canister 1.8 l, electropolished stainless steel)	144.4 ± 1.4 nmole/mole	canister #2

NIST Reference Standard	9.8 ± 0.05 μmol/mol	CLM006694
NMI Reference Standard	10.01 ± 0.04 μmol/mol	316511

For the audit at Cape Point the EMPA-WCC prepared two transfer standards by pressurising electropolished stainless steel "Rasmussen" canisters with air from the two CMDL Laboratory Standard CA03209 and CA03295, respectively. Prior to the filling process the canisters were repeatedly (10 times) pressurised and vented with ambient air for conditioning purposes. Then, each canister was repeatedly (5 times) pressurised and vented with air from the CMDL Laboratory Standards. The canisters were then analysed for the CO content and again after the audit. Over that period, the CO mixing ratio (ppb) had not changed noticeably.

The listed μmol/mol standards from NIST and NMI are checked against the CMDL standards by using dynamic dilution and analysis on an RGA-3 system.